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Structure and Bonding in Cyclic Isomers of BAl$_2$H$_n$^{m} ($n=3$–6, $m=-2$ to $+1$): Preference for Planar Tetracoordination, Pyramidal Tricoordination, and Divalency

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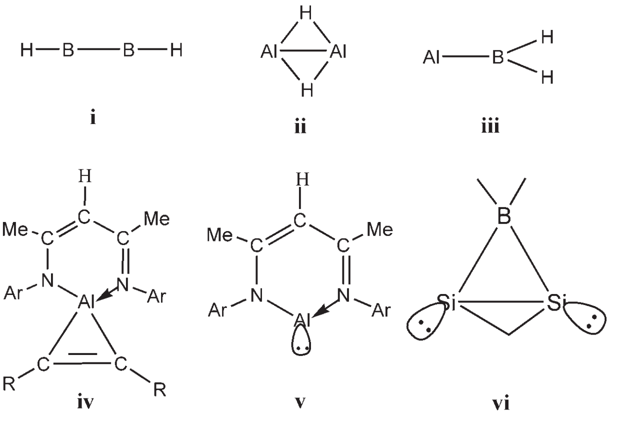
Abstract: The structure and energetics of cyclic BAl$_2$H$_n$^{m} ($n=3$–6, $m=-2$ to $+1$), calculated at the B3LYP/6-311+G** and QCISD(T)/6-311++G** levels, are compared with their corresponding homocyclic boron and aluminium analogues. Structures in which the boron and aluminium atoms have coordination numbers of up to six are found to be minima. There is a parallel between structure and bonding in isomers of BAl$_2$H$_3$$^{2-}$ and BSi$_2$H$_3$. The number of structures that contain hydrogens out of the BAl$_2$ ring plane is found to increase from BAl$_2$H$_3$$^{2-}$ to BAl$_2$H$_6$$^+$. Double bridging at one bond is common in BAl$_2$H$_5$ and BAl$_2$H$_6$$^+$. Similarly, species with lone pairs on the divalent boron and aluminium atoms are found to be minima on the potential energy surface of BAl$_2$H$_3$$^{2-}$. BAl$_2H_4$$^-$ (**2b**) is the first example of a structure with planar tetracoordinate boron and aluminium atoms in the same structure. Bridging hydrogen atoms on the B–Al bond prefer not to be in the BAl$_2$ plane so that the π MO is stabilised by π–σ mixing. This stabilisation increases with increasing number of bridging hydrogen atoms. The order of stability of the individual structures is decided by optimising the preference for lower coordination at aluminium, a higher coordination at boron and more bridging hydrogen atoms between B–Al bonds. The relative stabilisation energy (RSE) for the minimum energy structures of BAl$_2$H$_n$^{m} that contain π-delocalisation are compared with the corresponding homocyclic aluminium and boron analogues.

Keywords: ab initio calculations · aluminum · boron · bridging hydrogen · protonation

Introduction

Group 13 hydrides play a dominant role in chemistry in many ways. These include applications in organic synthesis,[1] organometallic catalysis,[2] materials chemistry[3] and possible hydrogen storage materials.[4] The availability of a variety of coordination numbers and geometries contribute to this versatile chemistry.[2b,5] Binary hydrides of boron and aluminium are especially interesting on account of their dramatic structural contrasts. For example, the global minimum structure of B$_2$H$_2$ is linear (Scheme 1, **i**),[6] whereas Al$_2$H$_2$ prefers a structure with two bridging hydrogens (Scheme 1, **ii**).[6a,7] Spectroscopy has shown that (dmp)BB(dmp) (dmp = 2,6-dimethylpiperidinato) has a linear RBBR geometry.[8] Al$_2$H$_2$ with a double-bridging hydrogen geometry has been identified by matrix IR spectra.[9] Mixed hydrides provide even



Scheme 1. R = SiMe$_3$, Ph; Ar = 2,6-iPr$_2$C$_6$H$_3$.

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more variety. The global minimum for $AlBH_2$ has a vinylidene-type structure[6a,10] similar to $Si{=}CH_2$ (Scheme 1, **iii**).[6a,11]

The recent interest in the chemistry of aluminium,[12] especially with the successful synthesis of compounds such as aluminocyclopropene[12,13] (Scheme 1, **iv**) and the aluminium analogue of carbene (Scheme 1, **v**) ($HC(CMeNAr)_2Al$; Ar = 2,6-$i$$Pr_2C_6H_3$),[12,14] indicate exciting possibilities for the future. The 2π-aromatic aluminium analogue (AlC_2H_3) of the cyclopropenyl cation has been suggested as one of the possible products in the reaction of AlCl monomers with acetylene in a solid argon matrix.[15]

We have already studied the structural variety possible for the 2π systems $B_3H_3^{2-}$, $Al_3H_3^{2-}$ and their protonated species.[16,17] Even more unusual structural variations are expected in heterocyclic rings. For example, the most stable structure of BSi_2H_3,[18] which is formally an isoelectronic neutral analogue of a cyclopropenyl cation, has a planar tetra-coordinate boron and a bridging hydrogen (Scheme 1, **vi**). We proposed an isolobal analogy between divalent silicon and trivalent boron to explain such unusual structures.[18,19] Schaefer and co-workers also reported similarities between silicon and aluminium hydrides (Al_2H_2 and Si_2H_2).[20] In view of the unusual structures encountered experimentally and theoretically of mixed compounds from Group 13 elements,[18–22] we study the three-membered system involving one boron and two aluminium atoms, starting with the 2π aromatic $BAl_2H_3^{2-}$. Although there is still no experimental evidence for these species, both theoretical and experimental studies of the electronic and geometrical structures of boron-doped bare aluminium metal clusters[23] and hydrogenated aluminium clusters[24] have been reported.

We present a comprehensive study of all the possible cyclic isomers of $BAl_2H_3^{2-}$ (**1**) and structures obtained by its sequential protonation, namely, $BAl_2H_4^-$ (**2**), BAl_2H_5 (**3**) and $BAl_2H_6^+$ (**4**). The study gives an insight to the structural varieties possible and their interconversions. We also probe the relative stability of these mixed hydrides brought by a cooperative effect of one boron and two aluminium atoms.

Computational Details

All structures derived as detailed below were optimised by means of the hybrid HF-DFT method, B3LYP,[25,26] based on Becke's three-parameter functional and including the Hartree–Fock exchange contribution with a non-local correction for the exchange potential proposed by Becke as well as the non-local correction for the correlation energy suggested by Lee et al. The 6-311+G** basis set was used for all calculations.[25] The nature of the stationary points was characterised by vibrational frequency calculations. The Gaussian 03 programme package was used for all calculations.[27] Fragment molecular orbital (FMO)[28] and natural bond orbital (NBO)[29] methods were used to analyse the bonding in a given structure. All the structures given in Figure 1 were also optimised with the QCISD(T) method using the 6-311++G** basis set.[25] A vibrational frequency analysis indicated that the structures were minima in energy at this level as well. The extent of variations in relative energies and structural parameters was minimal. The energetics of the structures shown in Figures 2–4 were checked by single-point calculations at this level.

Results and Discussion

The structures discussed in this article were obtained by isoelectronic replacement of the classical D_{3h} geometry of the cyclopropenyl cation by the Group 13 elements, that is, one CH group by BH and the other two CH groups by AlH groups. The charges and the number of additional hydrogens were adjusted to give two π electrons. Various starting geometries for $BAl_2H_3^{2-}$ were obtained by considering all possible combinations of bridging and terminal bonding positions. Similarly, the structures of the protonated species, $BAl_2H_4^-$, BAl_2H_5 and $BAl_2H_6^+$ were obtained by considering all possible combinations of bridging and terminal hydrogen occupancies. The optimised structures of $BAl_2H_3^{2-}$ and $BAl_2H_4^-$, BAl_2H_5 and $BAl_2H_6^+$, are given in Figures 1–4, respectively.

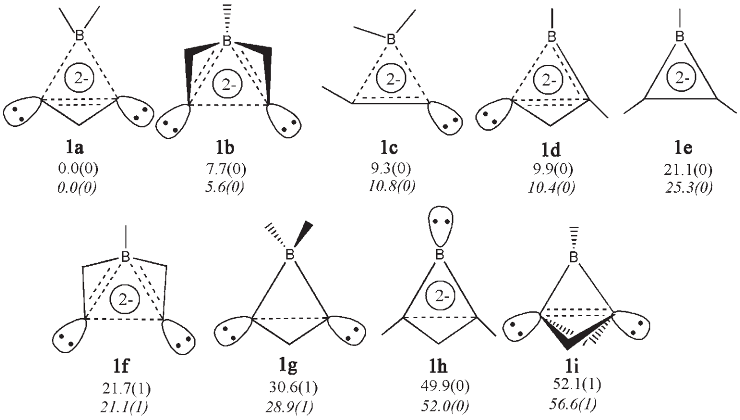

Figure 1. Structures **1a–i**, relative energies (kcal mol^{-1} at the B3LYP/6-311+G** level, values at the QCISD(T)/6-311++G** level in italics) and the number of imaginary vibrational frequencies (in parentheses) for $BAl_2H_3^{2-}$.

A variety of bonding situations exist in these complexes, ranging from the standard 2c–2e bonds, 3c–2e bonds involving a bridging hydrogen and two heavy atoms, 3c–2e bonds involving the three heavy atoms in the sigma plane and the familiar 3c–2e π-delocalisation. There are also several structures with lone pairs of electrons and planar tetra-coordinate arrangements. The structural drawings use the following convention to communicate visually the nature of the bonding as far as possible. A 2c–2e bond is represented by a solid line. A 3c–2e bond is represented by dotted lines, except those involving bridging hydrogen. Here, the connectivity between the hydrogen and the main-group element is represented by a solid line, and the connectivity between the main-group elements is represented by dotted lines. A 2π-electron delocalisation is represented by a solid circle inside the three-membered ring. These will be discussed once again while specific structures are introduced. Only the boron atom in the three-membered ring is labelled. The remaining two vertices are aluminium atoms. The relative energies and number of imaginary vibrational frequencies are

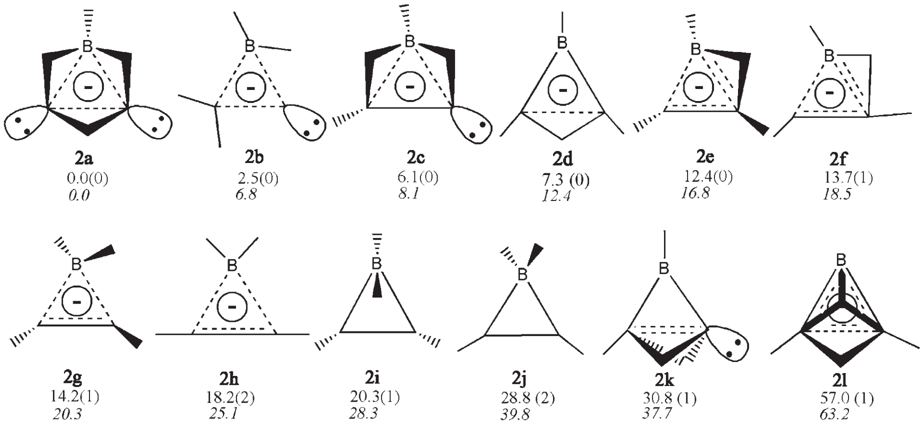

Figure 2. Structures **2a–l**, relative energies (kcal mol^{-1} at the B3LYP/6-311+G** level, values at the QCISD(T)/6-311++G** level in italics (single-point energy of B3LYP/6-311+G**-optimised geometry)) and the number of imaginary vibrational frequencies (in parentheses) for $BAl_2H_4^-$.

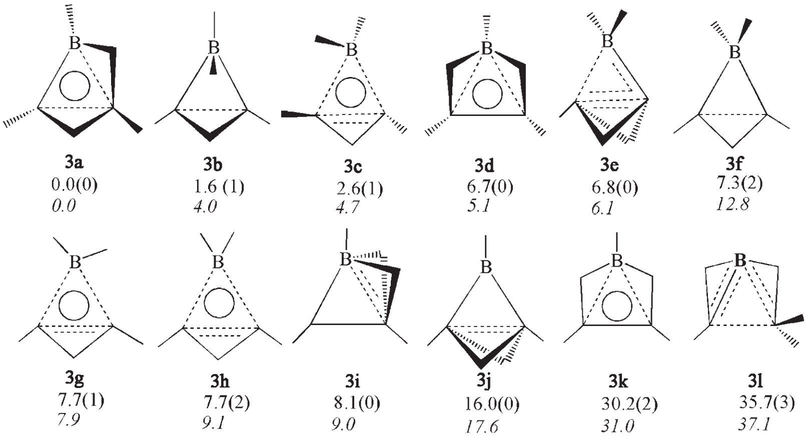

Figure 3. Structures **3a–l**, relative energies (kcal mol^{-1} at the B3LYP/6-311+G** level, values at the QCISD(T)/6-311++G** level in italics (single-point energy of B3LYP/6-311+G**-optimised geometry)) and the number of imaginary vibrational frequencies (in parentheses) for BAl_2H_5.

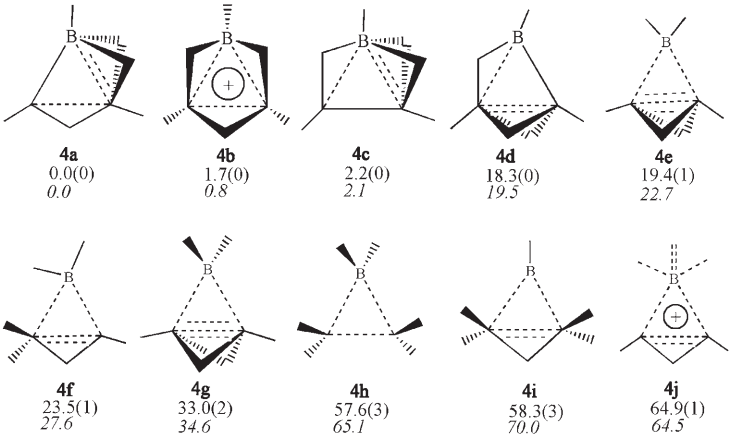

Figure 4. Structures **4a–j**, relative energies (kcal mol^{-1} at the B3LYP/6-311+G** level, values at the QCISD(T)/6-311++G** level in italics (single-point energy of B3LYP/6-311+G**-optimised geometry)) and the number of imaginary vibrational frequencies (in parentheses) for $BAl_2H_6^+$.

given below each structure in Figures 1–4. Important geometric parameters of the minimum energy structures are given in the Supporting Information. The discussions begin with the structures of $BAl_2H_3^{2-}$ (**1**). The structures obtained by protonation, $BAl_2H_4^-$ (**2**), BAl_2H_5 (**3**) and $BAl_2H_6^+$ (**4**), are discussed in this order. In view of the large number of minima obtained for **2**, **3** and **4**, these are discussed in relation to the isomers of $BAl_2H_3^{2-}$ (**1**). General comparisons are made at the end.

$BAl_2H_3^{2-}$: A variety of unusual bonding arrangements are observed among the many structures that have been found as energy minima. This study started with 28 different structures. Nine of them led to stationary points on the potential energy surface (PES), with six of them characterised as minima and three as transition states. The schematic representations of all nine isomers of $BAl_2H_3^{2-}$ are shown in Figure 1. The most stable structure, **1a**, has a planar tetra-coordinate boron atom. The two B–H bonds correspond to a conventional 2c–2e bond, the only two of its kind in this structure. These two bonds are represented by solid lines (Figure 1). The third hydrogen is bridged between aluminium atoms and is represented by solid lines between the hydrogen and the aluminium atoms and a dotted line between the two aluminium atoms. There is an in-plane 3c–2e bond that binds the three heavier elements together and is represented by dotted lines between the three heavier elements. Thus, there are two dotted lines between the aluminium atoms. There is a lone pair on each aluminium atom and is indicated by a half dumb-bell with two dots inside. The 2π-electron delocalisation is represented by a solid circle and the charge of the molecule (−2) is given inside the solid circle.

An NBO analysis of **1a** supports this description. A similar structure with planar tetra-coordinate aluminium is shown to be the global minimum in $Al_3H_3^{2-}$.[16] The corresponding planar tetracoordinated homocyclic boron analogue, $B_3H_3^{2-}$ is 58.12 kcal mol^{-1} higher in energy than its global minimum structure of symmetry D_{3h}.[16] The reversal of the relative stability of the structure with planar tetracoordination by the replacement of two boron by aluminium is remarkable. An isomer similar to **1a** is the global minimum for the neutral isoelectronic BSi_2H_3.[18] An isolobal analogy that we had proposed between divalent silicon and trivalent boron is extended to make the link between silicon and aluminium and helps in making the connection between **1a** and the isostructural BSi_2H_3.[18,19] Geometry optimisation of a structure with planar tetracoordination around aluminium leads to **1c**, which contains di- and tricoordinate aluminium atoms. This indicates the reluctance of aluminium for sp^3 hybridisation and higher coordination in comparison to boron.

The next stable structure, **1b**, has a penta-coordinate boron atom. It has one terminal B−H bond and bridging hydrogen atoms on each B−Al bond. All the three hydrogen atoms are out of the BAl_2 plane. Following the convention described earlier for structural representation, structure **1b** has one 2c–2e B−H bond, one 3c–2e bond between Al-B-Al, two 3c–2e bonds involving B-H-Al hydrogen bridges and one lone pair on each aluminium atom. Although there is considerable mixing between the original π MOs of the planar structure and the s orbital of the bridging hydrogens, it is conceptually better to treat this as a π MO. The planar alternative, **1f** is a transition state for the conversion of **1b** to the equivalent structure where the direction of the bridging and the terminal hydrogens are reversed. The instability of **1f** is mainly attributable to the non-bonded interaction between bridging hydrogen atoms and the terminal hydrogen atom. The distance between these two hydrogen atoms in **1f** is 1.90 Å at the B3LYP/6-311+G** level of theory. It increases to 2.00 Å in **1b**. The H–H distances increase substantially in the homocyclic aluminium analogue of **1f**, which is a minimum.[16] A similar structure is also calculated to be a minimum for the isoelectronic $Si_3H_3^+$,[30] where unfavourable H–H interactions are not anticipated. However, similar structures of BSi_2H_3 and $B_3H_3^{2-}$, containing a penta-coordinate boron, have one imaginary frequency. Each of them leads to the minimum energy structure corresponding to **1b**. The structural similarities of $BAl_2H_3^{2-}$ and BSi_2H_3 in **1a**, **1b** and **1f** further illustrate the resemblance of silicon and aluminium hydrides (SiH and AlH^-). The bridging hydrogen atoms connected to boron in **1b** and in BSi_2H_3 (similar structure to **1b**) demonstrate the preference of the out-of-plane bridging position. Similarly, several non-planar structures with stabilised π MOs are revealed in this study. A comparison of the stabilisation of the π MOs in going from the planar to the non-planar structures and their contribution to the total energies are given below.

Structure **1c** is not observed in homocyclic boron and aluminium analogues.[16] Here, the BH_2 group and the terminal hydrogen atom of aluminium are bent towards each other and it has a planar, tetracoordinate boron atom. Important bonding interactions in this molecule can be visualised by interacting H-Al-Al and BH_2 fragments. The sp-hybrid lone pair of AlH is donated to the empty in-plane p orbital of the bare aluminium atom (Figure 5a). This results in a 2c–2e bond between the aluminium atoms. NBO analysis also supports this description. The second interaction (Figure 5b) is the hyperconjugative donation from the in-plane bonding combination of a BH_2 group orbital to the empty antibonding Al-H σ* orbital. This explains the elongation of the B−H (1.23 Å) and Al−H bond lengths (1.68 Å) and tilting of the BH_2 group towards the aluminium having the hydrogen atom. An NBO analysis shows that the stabilisation energy arising from hyperconjugation is 4.5 kcal mol^{-1}. In addition, there is one delocalised π MO, two 2c–2e B−H bonds and one 2c–2e Al−H bond.

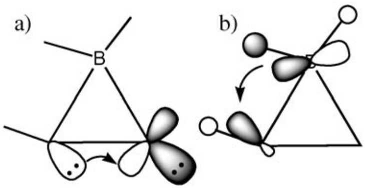

Figure 5. Representations of a) 2c–2e Al−Al bond and a lone pair on Al and b) a hyper-conjugative B−H and Al−H interaction in **1c**.

Structure **1d** has a bridging hydrogen atom between two aluminium atoms, one terminal B−H bond and one terminal Al−H bond. Homocyclic aluminium and boron analogues of **1d** are not stable.[16] A structure similar to **1d** in which hydrogen bridges boron and silicon is a minimum for BSi_2H_3.[18] Structure **1d** has an elongated Al−Al bond (2.69 Å) and the shortest HB−AlH bond (2.00 Å) among all structures studied here. This molecule can be considered to be a combination of two fragments such as HAl-H-Al and BH. The mono-bridged HAl-H-Al and its silicon analogues are characterised as minima.[20] The HAl-H-Al fragment donates its sigma lone pair to the in-plane empty p orbital of the BH fragment (Figure 6a). This forms a bent bond and results in a short HB−AlH bond length (2.00 Å).[31] A noteworthy feature in the HAl-H-Al fragment is the hyperconjugative donation from the in-plane bonding combination of an AlH_2 fragment into the empty p orbital of the aluminium atom to form a weak 3c–2e Al-H-AlH bond. This results in elongation of the Al−H bond lengths (1.92 Å, 1.72 Å). In addition, it contains 2c–2e B−H and Al−H bonds and a delocalised π MO over the ring.

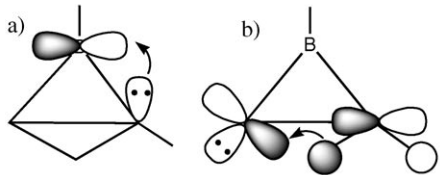

Figure 6. Representations of a) a 2c–2e bent B−Al bond and b) a hyper-conjugative 3c–2e Al-H-Al bond and a lone pair on Al in **1d**.

The classical structure **1e** has three terminal hydrogen atoms on each atom of the three-membered ring. It is 21.0 kcal mol^{-1} higher in energy than the global minimum structure, **1a**. The corresponding aluminium analogue is 1.8 kcal mol^{-1} higher in energy than its global minimum structure.[16] The Al−Al and B−Al distances are shorter than their corresponding single bond lengths and longer than double bonds. The MOs of **1e** are similar to the classical Walsh orbitals of the cyclopropenyl cation and a delocalised π MO over the ring.

Structure **1g** is non-planar with a tetrahedral arrangement around boron and a bridging hydrogen atom between the aluminium atoms. It is obtained by twisting the BH_2 group of **1a** by 90°. This structure is a first-order saddle point and 30.6 kcal mol^{-1} higher in energy than **1a**. The imaginary vibrational frequency vector of **1g** leads to a ring-opened structure.

Structure **1h** is the highest energy minimum that we have obtained on the PES of $BAl_2H_3^{2-}$: it is 49.9 kcal mol^{-1} higher in energy than **1a**. A similar structure is a first-order saddle point for homocyclic boron analogue, but the second most stable structure for the aluminium analogue.[16] Both the B−Al and the H-bridged Al−Al bond lengths in **1h** are shorter compared to those in **1a**, with the exception of the Al−H_b (bridging hydrogen). The electronic structure of **1h** has one 3c–2e Al-H-Al bridge to bind the two Al atoms. As shown in Figure 7b, the Al-H-Al bridge has a direct radial overlap between aluminium atoms, which results in a shorter Al−Al bond (2.47 Å). Similarly, **1h** has two 2c–2e B−Al bonds. It is formed by the donation of a lone pair of electrons from the aluminium atom to the empty sp^2-hybrid orbital of boron (Figure 7a) and results in a shortening of the B−Al bonds (2.09 Å). In addition, **1h** has two 2c–2e Al−H bonds, a lone pair on B and a delocalised π MO over the ring. The lone pair on boron imparts an extremely high energy to the system. The other structural alternative of **1h**, in which the aluminium atom has a lone pair of electrons, on geometry optimisation, converges to **1c**, which is unusual.

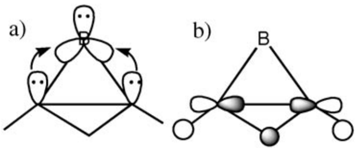

Figure 7. Representations of a) 2c–2e B−Al bonds and a lone pair on boron and b) a 3c–2e Al-H-Al bond in **1h**.

The highly unstable cyclic structure of $BAl_2H_3^{2-}$ (**1i**), which contains two hydrogen atoms bridging the Al−Al bond and a pyramidal boron atom, is a transition state corresponding to a hydrogen shift from one aluminium atom to another in **1d**. The barrier for the hydrogen shift in **1d** is 42.2 kcal mol^{-1}. A similar structure for homocyclic boron and aluminium analogues represents second-order and first-order saddle points, respectively.[16] Interestingly, the isoelectronic BSi_2H_3, which has a planar arrangement around boron, is a minimum at the QCISD(T)/6-31G* level.[18]

In view of the large number of structures within a small range of energy, these structures were also optimised at the QCISD(T)/6-311++G** level of theory. There were minimal differences in relative energies. The geometric parameters also did not change dramatically.

Studies of the structure and bonding of various $BAl_2H_3^{2-}$ isomers show similarities to BSi_2H_3 and prompts the familiar isolobal analogy between SiH and AlH^-. The relative stabilities of the $BAl_2H_3^{2-}$ isomers predict a preference for lower coordination at the aluminium atoms and a higher coordination at boron. Generally, greater preference is given to structures with lone pairs on each aluminium compared to those having fewer lone pairs. Each of the $BAl_2H_3^{2-}$ isomers provides several sites for protonation. Structures resulting from the sequential protonation of $BAl_2H_3^{2-}$ provide interesting bonding characteristics. Their electronic structures and inter-relationships are discussed in the next section.

$BAl_2H_4^-$, BAl_2H_5 and $BAl_2H_6^+$: The relative energy and the number of imaginary frequencies of all the isomers of $BAl_2H_4^-$, BAl_2H_5 and $BAl_2H_6^+$ are shown in Figures 2–4. The number of minimum energy structures decreases from $BAl_2H_3^{2-}$ (six) to $BAl_2H_6^+$ (four). There are several unusual bonding arrangements in these compounds. For example, structures **1a**, **1c**, **2b** and **4d** have a planar tetracoordinate arrangement on boron. This is attributable to the electron deficiency of boron and, as a result, it becomes more flexible to form multicentre bonding in comparison with carbon.[32] It is important to note that **1a** is the global minimum structure on the PES of $BAl_2H_3^{2-}$. The extra stability of **1a** is attributable to a combination of effects, such as the tendency toward divalent aluminium atoms, a 3c–2e σ-Al-B-Al bond and a two π-electron delocalisation over the ring.

Structures **1b**, **2a**, **2c**, **3d**, **3i**, **4a** and **4b** have a penta-coordinate arrangement around the boron atom. A hexa-coordinate boron is seen in structure **4c**. Planar tetra-coordinate aluminium is present in **1e**, **1h**, **2b**, **2d**, **4a** and **4c**. A planar tetracoordinate boron atom and aluminium in the same structure is observed in **2b**.

The easiest way to understand most of these structures is to treat them as protonated species obtained from one or the other isomers of $BAl_2H_3^{2-}$ (Figure 8). There are six minima available for $BAl_2H_3^{2-}$. The arrows in Figure 8 indicate the direct structural relationship that exists between all the minimum energy structures of $BAl_2H_3^{2-}$, $BAl_2H_4^-$, BAl_2H_5 and $BAl_2H_6^+$ via the protonation route. Several direct connections appear to be missing. This is because many obvious protonation paths lead to higher-order stationary points. Even though these are followed up to their eventual minima, only the minimum energy structures are given here.

For example, let us consider the protonation pathway (**1b**→(**2a**)**2c**→**3d**→**4b**). A molecular orbital representation of the protonation route is shown in Figure 9 (the hydrogen atoms have been omitted in this scheme for reasons of clarity). As described above, **1b** has two 3c–2e Al-H-BH bridges and one 3c–2e Al-B-Al ring and one 2c–2e B−H bond. In addition, it has lone pairs on each Al atom and a bent π MO between two aluminium atoms (Figure 9). Both lone

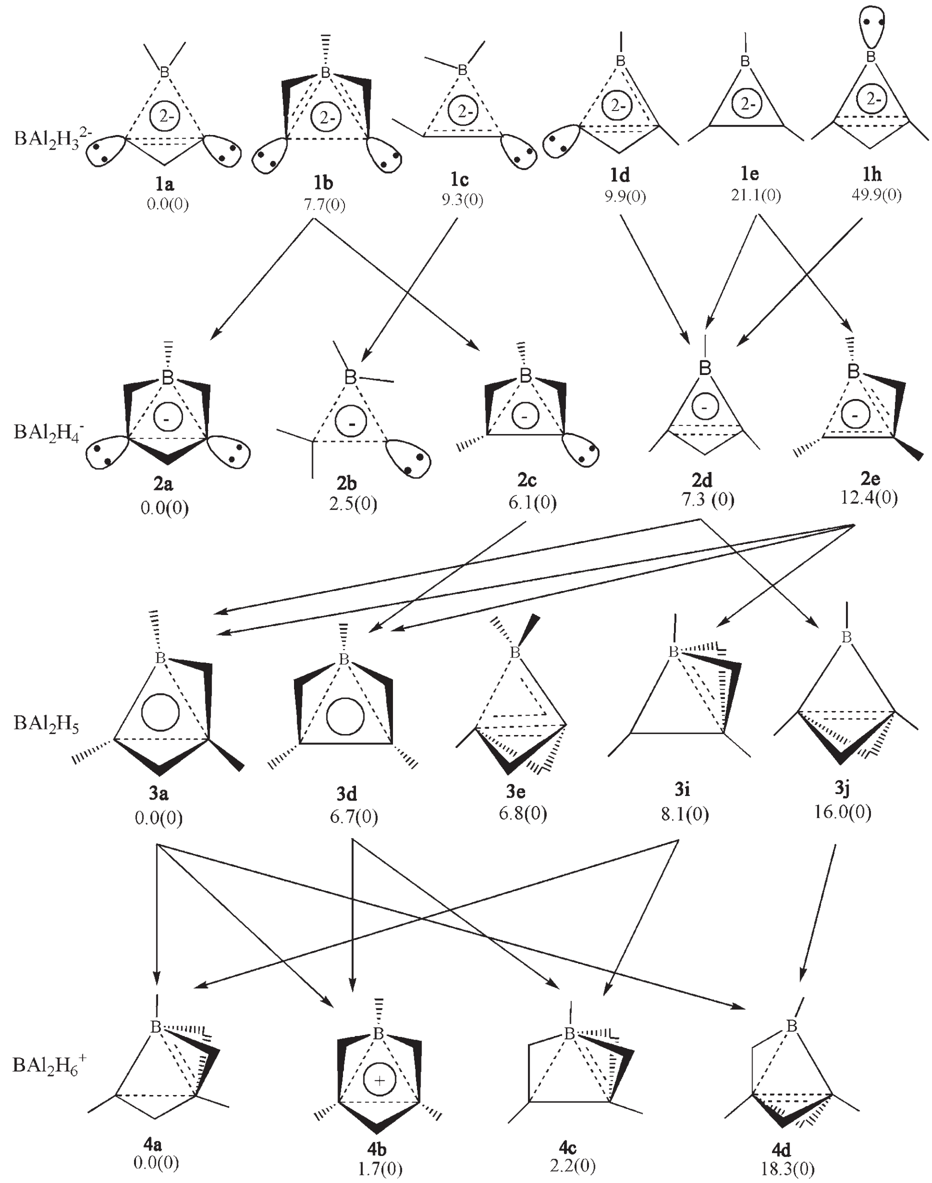

Figure 8. Protonation route of $BAl_2H_n^m$ ($n=3$–6, $m=-2$ to $+1$) isomers.

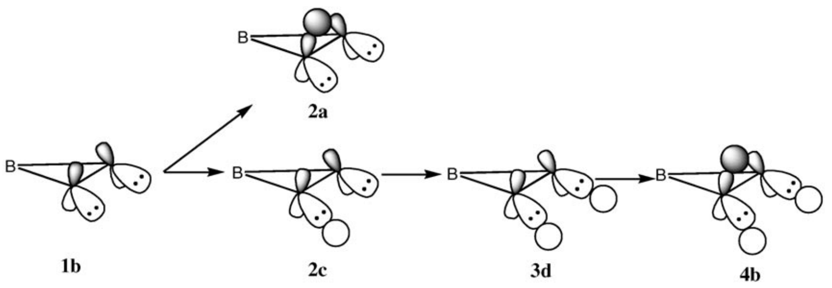

Figure 9. Schematic molecular orbital representation of the protonation of (**1b**→(**2a**)**2c**→**3d**→**4b**). Some of the hydrogen atoms are left out for clarity. The structures are given in Figures 1–4.

pairs and bent π MO are out of the plane of the three-membered ring and directed away from each other.

The proton can be added to the more reactive nucleophilic centre of **1b**. These are the lone pairs on each aluminium atom or the bent π MO of the Al–Al bond. The interaction of H^+ with a lone pair on one of the aluminium atoms results in **2c**, which has the terminal Al–H bond out of the ring plane. A similar structure is not observed for homocylic boron or aluminium analogues. The addition of the H^+ to the bent π MO of the Al–Al bond in **1b** results in **2a**, the cyclic global minimum structure of $BAl_2H_4^-$. This structure has a lone pair on each aluminium atom. The corresponding homocyclic aluminium analogue is 5.4 kcal mol^{-1} (at the B3LYP/6-31g* level) higher in energy than its global minimum structure,[16] which is similar to the structure of **2e**. The structure of **2c**, which has a lone pair on one of the aluminium atoms, is 6.1 kcal mol^{-1} higher in energy than **2a**, which has a lone pair on each aluminium atom. There are no stable structures that result from the protonation of **2a**. This supports our hypothesis that the more reactive nucleophilic centre is a π MO rather than the lone pair on the aluminium atom.

The addition of a proton to **2c** results in another terminal Al–H bond (**3d**). This terminal Al–H bond is also not in the ring plane. A structure similar to **3d** is the global minimum for the homocyclic aluminium analogue, while its planar alternative is the global minimum for the homocyclic boron analogue. The shortest distance between a terminal hydrogen and a bridging hydrogen is 2.00 Å in planar B_3H_5. A similar distance is observed in **1b**. The planar alternative to **3d** is **3k**, which is a second-order saddle point on the PES. The distance between bridging and terminal hydrogens on boron in **3k** is 1.90 Å at the B3LYP/6-311+G** level of theory. This increases to 2.02 Å in **3d**. Optimisation in the direction of one of the imaginary vibrational frequency vectors of **3k** leads to structure **3d**. The addition of another proton on **3d** results in bridging between two aluminium atoms (**4b**). Here, the three bridging hydrogens are on one side of the ring and the three terminal hydrogens are on the other side. This structure is similar to the global minimum structure of $B_3H_6^+$.[16,17a] Here, the π MO is stabilised further by mixing with the in-plane combination of the three s orbitals of the bridging hydrogens. A similar structure is the third most stable among the isomers of $Al_3H_6^+$.[16] The addition of H^+ to **3d** also results in **4c**, with three terminal and three bridging hydrogens. Two of the latter hydrogens bridge the same B–Al bond. The third one bridges the next B–Al bond, and is in the BAl_2 plane.

The global minimum structures **1a** and **2a** do not have any protonation route that retains the same structural details. The higher-order saddle point structures eventually converge to other structures. Structure **2b** is unusual in that it contains both planar tetracoordinate boron and aluminium atoms. It can be obtained by protonation at the lone pair on aluminium atom in **1c** (Figure 5a).

Protonation of structures **1d**, **1e** and **1h** leads to the same product **2d**, which is formed by the interaction of H^+ with the lone pair on the aluminium atom in **1d**, the Al–Al in-plane sigma bond in **1e** and the lone pair on the boron atom in **1h**. This structure is a minimum for the homocyclic boron analogue and a first-order saddle point for the aluminium analogue. The electronic structure of **2d** consists of one 2c–2e B–H, two Al–H and two B–Al bonds, a 3c–2e Al-H-Al bond and a delocalised π MO. Protonation at the B-Al in-plane sigma bond of **1e** results in **2f**. It is a transition state for the interconversion of **2e**, and the energy barrier for the interconversion is 1.3 kcal mol^{-1}. In **2e**, all the terminal and bridging hydrogens are out of the plane of the three-membered ring, and the tricoordinate aluminium atom has pyramidal geometry. This is to be compared to the structure of $SiCBH_5$ with a pyramidal tricoordinate boron[21] and its heavier analogues[16] in an unconstrained geometry. The classical structure **2j**, which has two imaginary vibrational frequencies, is considerably higher in energy. One of the imaginary vibrational frequencies leads to **2g** where the p orbitals of aluminium are brought to bonding. Although **2g** is a transition state, a structure similar to **2g** is a minimum in the PES of the homocyclic $Al_3H_3^{2-}$. Further twisting of the BH_2 group in **2g** results in a bridging hydrogen atom at the B–Al bond (**2e**). The energy difference between **2e** and **2g** is only 1.8 kcal mol^{-1} at the B3LYP/6-311+G** level of theory. The anti-van't Hoff structure **2h** is a second-order saddle point. Optimisation in the direction of the first imaginary vibrational frequency leads to **2f**, which is a transition state for the interconversion of **2e**.

Structures **2k** and **2l** are first-order stationary points. Optimisation in the direction of the imaginary vector of **2l** leads to structure **2d**. Structure **2k**, which has two bridging hydrogen atoms on the Al–Al bond, is a transition state that leads to **2b**.

The global minimum structure of BAl_2H_5, **3a**, can be obtained by protonation of **2d** and **2e**. All the terminal and bridging hydrogens are out of the plane of the three-membered ring. Structures **3i** and **3j** are formed by the addition of two protons to the π orbital at B–Al and Al–Al, respectively, in **1e**. The preference for hydrogen bridging at B–Al over Al–Al is reflected in the energy difference of 7.9 kcal mol^{-1} between **3i** and **3j**. Structure **3e** is an unusual structure, in that there is tetrahedral coordination at boron, which is not otherwise seen in this series. The electronic structure of **3e** consists of the two 2c–2e B–H bonds, one 2c–2e Al–H bond, one 2c–2e B–Al bond and two 3c–2e bonds between Al-Al-H and one 3c–2e bond between B-Al-Al.

Protonation of **2d** can also result in second-order saddle point structures, **3f** (van't Hoff) and **3h** (anti-van't Hoff). The first imaginary vibrational frequency of **3f** leads to structure **3b**. This is a transition state for the shifting of the bridging hydrogen atom between two B–Al bonds in **3a**. Similarly, the first imaginary vibrational frequency of **3h** leads to structure **3c**. Optimisation of structure **3c** in the direction of the frequency vector leads to structure **3a**. Structure **3g** is also a transition state for the out-of-plane distortion of hydrogen atoms in **3a**.

Protonation of the global minimum structure, **3a**, gives three stable structures, **4a**, **4b** and **4d**, depending on the protonation position. Structures **4a**, **4c** and **4d** have two doubly bridged out-of-plane hydrogen atoms in one bond and one in-plane bridging hydrogen atom. All terminal hydrogen atoms are in the same plane of the ring. The significant molecular orbitals contributing to the bonding in **4a**, **4c** and **4d** are shown in Figure 10. The preference for hydrogen bridging at B–Al over Al–Al explains the stability of **4a** and **4c** over **4d**. The higher stability of **4a** over **4c** is attributable to the preference of the in-plane bridging hydrogen at the Al–Al bond rather than at the B–Al bond. The energies of structures **2**, **3** and **4** were evaluated by a single-point calculation at the QCISD(T)/6-311++G** level using B3LYP/6-311+G** geometries. The relative energies (given in Figures 2–4) did not change considerably.

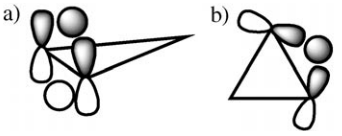

Figure 10. Representations of a) two out-of-plane bridging hydrogens and b) an in-plane bridging hydrogen in **4a**, **4c** and **4d**.

Seven non-planar structures of the 43 structures given in Figures 1–4 appear to have an option for a planar structure with all hydrogens remaining in the BAl_2 plane. Yet these seven are all non-planar, despite the fact that in the planar structures, there will be an undisturbed π MO. Obviously, significant stabilisation is obtained by mixing the s orbital of the bridging hydrogens and the in-plane p orbitals with the π orbital. The extent of this stabilising effect is gauged by a correlation diagram (Figure 11) connecting the π-MO energy at the planar geometry (middle of the plot, adjusted to zero) and the same MO in the non-planar geometry (left side) obtained from ab initio MO calculation at the B3LYP/6-311+G** level of theory using the Gaussian03 programme package. The relative energies correspond to twice the MO energy to reflect the occupancy of two electrons. As the number of bridging hydrogen atoms increases, the stabilisation of the π MO also increases. Maximum stabilisation of the π MO is seen for **4b** and **2a**, both having three bridging hydrogens. Structures with two bridging hydrogens **1b**, **2c**, **3a** and **3d** have less stabilisations of the π MO on distortion from the planar structure. The least stabilisation of the π MO is calculated for structure **2e** with one bridging hydrogen.

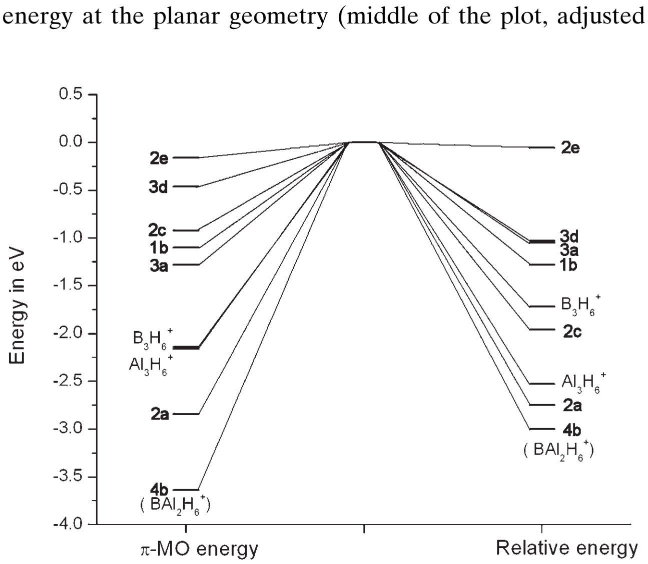

Figure 11. Stabilisation of the π-MO of the structures having out-of-plane hydrogen bridges (left side) in comparison to corresponding planar structures from ab initio MO calculation at B3LYP/6-311+G** level of theory using Gaussian03 programme package. The relative energies of the structures in relation to the planar arrangement are shown on the right side. Relative π-MO and total energies of the homocylic boron and aluminium analogues of structure **4b** are also shown.

The extent of the π-MO contribution to the stabilisation of the non-planar structure is indicated by the parallel behaviour of the total energy that is also plotted in Figure 11 (right-hand side). However, it is not only stabilisation of the π MO that controls the energetics. Another contribution to decreasing the energy of the non-planar structure is the H–H repulsion that exists in the planar structure. This is relieved in the non-planar structure. The steric repulsion is maximum when there are three bridging hydrogens in the planar structure, explaining the non-linear increase in energy with increasing number of bridging hydrogens. This is to be compared to the planar structures preferred for $B_3H_4^-$ (one bridging hydrogen) and B_3H_5 (two bridging hydrogens). Addition of the third bridging hydrogen as in $B_3H_6^+$ makes the structure non-planar, with the three bridging hydrogens pushed away from the B_3 plane and opposite to the three terminal B–H bonds. When the π interactions in the planar arrangements are weak, the tendency toward non-planarity increases. Thus, the structure with one bridging hydrogen ($Al_3H_4^-$) and two bridging hydrogens (Al_3H_5) are lowest in energy on their PES. Though a structure with three bridging hydrogens is a minimum in energy on the PES of $Al_3H_6^+$, the lowest-energy isomer has four bridging hydrogens. This does not mean that there is no minimum energy structure with in-plane bridging hydrogens. Structures **1d** and **2d** are planar structures with one bridging hydrogen each and show the delicate balance of the various factors that bestow stability to a structure.

The relative stabilisation energy (RSE) for the minimum energy structures that contain π delocalisation is compared with the corresponding homocyclic aluminium and boron analogues by means of Equations (1)–(7) (Figure 12). The sum of the Al–Al, B–B and B–Al bond energies (see [Eqs. (8) and (9)] in Figure 12) would indicate that all reactions are endothermic by 17.7 kcal mol^{-1}. However, there are other factors involved: the high negative value of ΔE for **1a** is attributable to the more preferential position of lone pair on aluminium compared to the boron atom. It also has a contribution from the stronger B–H (≈93 kcal mol^{-1}) in comparison with the weaker Al–H bonds (≈69.2 kcal mol^{-1}). The positive values of **1e**, **2d**, **3a** and **3d** are the result of less π delocalisation through differential radial extension of the p orbital of aluminium and the boron atoms.

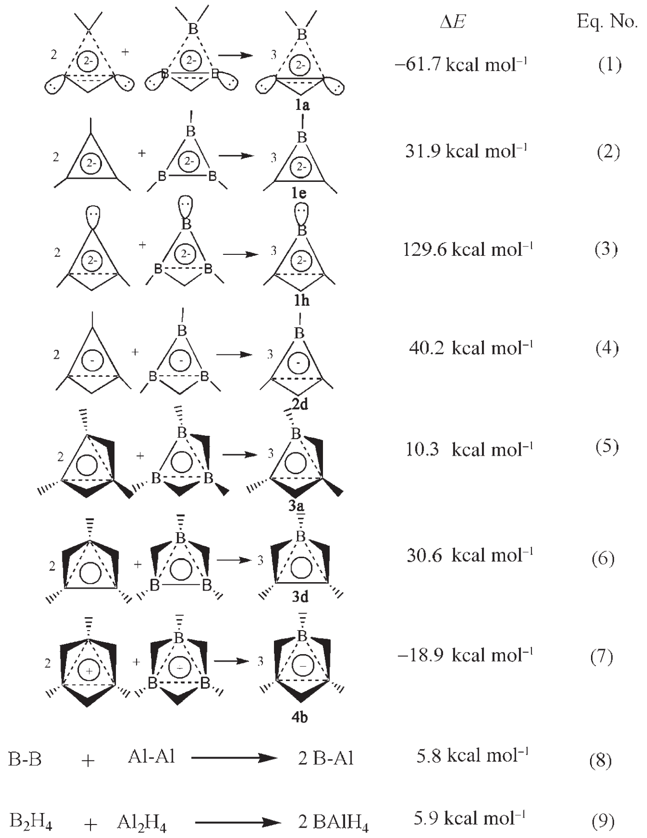

Figure 12.

The stronger B-H-B bridge in relation to the Al-H-Al bridge has also contributed to the endothermicity of **1h**, **2d**, **3a** and **3d**. The instability of the lone pair on the boron atoms leads to the high dramatic positive value for **1h**. The stabilisation obtained by mixing the π MO with the in-plane σ MO is larger for the **4b** structure than for the corresponding homocyclic boron and aluminium analogues (Figure 11). This results in exothermicity of Equation (7) (Figure 12).

Conclusion

The structure and bonding of $BAl_2H_n^m$ ($n=3$–6, $m=-2$ to $+1$) species are compared with their corresponding homocyclic boron and aluminium analogues. $BAl_2H_3^{2-}$ shows similarities to BSi_2H_3 with respect to its geometrical and bonding pattern. There are several unusual geometrical and bonding patterns, such as planar tetracoordinate boron and aluminium atoms in the same ring in $BAl_2H_4^-$ (**2b**) and divalent boron with a lone pair (**1h**), which are common among them. The variety of coordination modes and their interconversions are important in catalytic processes. The bridging hydrogen at the B−Al bond prefers to be outside the plane of the three-membered ring. The stabilisation of the π MO is a major contributor with respect to a preference for non-planar structures with H bridging. As the number of bridging hydrogen atoms increases, the stabilisation of the π MO also increases. A similar structure with two bridging hydrogen atoms at the Si−Si bond (Si_2H_2) has been observed experimentally. The most stable structures are the result of lower coordination of aluminium, higher coordination on boron and more bridging hydrogen atoms between B−Al bonds. The relative stabilisation energy (RSE) of $BAl_2H_n^m$ isomers depends on all these factors.

The synthesis of several derivatives of BC_2H_3 and $B_2CH_3^-$ and the recent work on aluminocyclopropene has provided new impulses in the study of mixed hydrides of Group 13 and 14 elements. Experimental observation of $BAlH_6$ and $BGaH_6$ has provided new insights to the mixed hydrides of Group 13. The large variety of novel structural patterns of the mixed hydrides of Group 13 elements presented here invite experimental verification.

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